Magnetic and Spectroscopic Characterization of Copper(II) Toluate Adducts with Substituted Piperidines

B. S. Manhas [a] , A. K. Sardana [a] & S. B. Kalia [b]

[a] Department of Chemistry , Punjabi University , Patiala, 147-002, India

[b] Department of Chemistry , Himachal Pradesh University , Shimla, 171-005, India
Published online: 15 Feb 2007.

PLEASE SCROLL DOWN FOR ARTICLE

Magnetic and Spectroscopic Characterization of Copper(II) Toluate Adducts with Substituted Piperidines

B. S. Manhas,[1] A. K. Sardana,[1] and S. B. Kalia[2],*

[1]Department of Chemistry, Punjabi University, Patiala, India
[2]Department of Chemistry, Himachal Pradesh University,
Shimla, India

ABSTRACT

New copper(II) toluate complexes with saturated monoheterocyclic bases, substituted piperidines, of the type $Cu(OOCR)_2L$ (where R = 2-, 3-, or $4\text{-}CH_3C_6H_4$ and L = 1-methyl-, 1-ethyl- or 2,6-dimethylpiperidine) have been synthesized and characterized by elemental analyses, IR, electronic reflectance and EPR spectral and magnetic susceptibility measurement studies. All of these complexes show antiferromagnetic behaviour. The spin exchange parameter, $-2J$, for three of these complexes has been evaluated from EPR measurements at different temperatures, which corresponds to axial binuclear copper(II) complexes with S = 1.

*Correspondence: S. B. Kalia, Department of Chemistry, Himachal Pradesh University, Shimla 171 005 India; E-mail: sanjay263@rediffmail.com.

519

INTRODUCTION

A literature survey reveals that there has been considerable interest in the chemistry of metal(II) carboxylates and their complexation properties with nitrogen and oxygen donor ligands[1−7] and only some workers have examined the role of ''steric hindrance'' or electronic nature of the substituent group on pyridine type ligands[3,5−10] in their complexation behaviour with cobalt(II), nickel(II) and copper(II) carboxylates. No such systematic efforts have yet been made for saturated heterocyclic bases. Thus, in the present work a study of the complexation properties of substituted piperidines with copper(II) toluates has been undertaken.

EXPERIMENTAL

The bases, 1-methylpiperidine, 1-ethylpiperidine and 2,6-dimethylpiperidine (Aldrich Chemicals or K and K Laboratories) were dried by refluxing over sodium hydroxide beads. The colourless liquids obtained after distillation were stored over sodium hydroxide beads.

Preparation of Copper(II) Toluates
(*ortho*-, *meta*- and *para*-)

To the solution of toluic acid (Sisco) (5 g, 36.72 mmol) in the minimum quantity of acetone (30 mL) was added drop-wise with stirring at room temperature a solution of sodium hydroxide (1.469 g, 36.72 mmol) in distilled water (8 mL). The pH of the resulting solution of sodium toluate was then adjusted to 5 by adding an appropriate amount of toluic acid. A filtered solution of copper(II) sulfate pentahydrate (4.585 g, 18.73 mmol) in distilled water (30 mL) was then added to the stirred solution of sodium toluate. The precipitate, thus obtained, was filtered, washed with distilled water and dried in air. It was then dried at 110 °C for two hours.

Preparation of Complexes

Copper(II) toluate (1 g, 2.99 mmol) was suspended in diethyl ether (30 mL) in a round-bottom flask. A solution of the stoichiometric amount or 50% excess (Table 1) of heterocyclic base in the same solvent (15 mL) was added drop-wise after successive intervals of 10 min. in a total period of about 2.5 h to the continuously stirred suspension of copper(II) toluate. Coloured solutions of the adducts (Table 1) were obtained as the solid copper(II) toluate dissolved. The solid adducts of the bases separated after

Table 1. Elemental analysis data, colors and particulars of the method of preparation of the complexes.

Compound (composition) [formula weight]	Yield (%)	Elemental analysis found (%) (calculated (%))				Color	S.a./excess[a]	Dec. p. (°C)
		Cu	C	H	N			
$Cu(OOCC_6H_4CH_3\text{-}4)_2(1\text{-MePipd})$ $(C_{22}H_{27}NO_4Cu)$ [422.5]	90	14.83 (14.68)	60.78 (61.02)	6.11 (6.29)	2.98 (3.23)	Bluish green	Excess	245
$Cu(OOCC_6H_4CH_3\text{-}4)_2(1\text{-EtPipd})$ $(C_{23}H_{29}NO_4Cu)$ [446.5]	85	13.80 (14.22)	62.04 (61.80)	6.31 (6.54)	3.02 (3.13)	Bluish green	Excess	240
$Cu((OOCC_6H_4CH_3\text{-}4)_2(2,6\text{-Me}_2Pipd)$ $(C_{23}H_{29}NO_4Cu)$ [446.5]	65	14.65 (14.22)	61.30 (61.80)	6.56 (6.54)	3.32 (3.13)	Sky blue	S.a.	180
$Cu((OOCC_6H_4CH_3\text{-}3))_2(1\text{-MePipd})$ $(C_{22}H_{27}NO_4Cu)$ [422.5]	85	14.83 (14.68)	60.91 (61.02)	6.09 (6.29)	2.97 (3.23)	Green	Excess	240
$Cu(OOCC_6H_4CH_3\text{-}3)_2(1\text{-EtPipd})$ $(C_{23}H_{29}NO_4Cu)$ [446.5]	80	13.84 (14.22)	61.45 (61.80)	6.17 (6.54)	2.74 (3.13)	Greenish-blue	Excess	205
$Cu((OOCC_6H_4CH_3\text{-}3)_2(2,6\text{-Me}_2Pipd)$ $(C_{23}H_{29}NO_4Cu)$ [446.5]	60	13.86 (14.22)	61.37 (61.80)	7.00 (6.54)	2.70 (3.13)	Blue	S.a.	190
$Cu((OOCC_6H_4CH_3\text{-}2)_2(1\text{-EtPipd})$ $(C_{23}H_{29}NO_4Cu)$ [446.5]	75	14.53 (14.22)	61.53 (61.80)	6.13 (6.54)	2.75 (3.13)	Dark-green	Excess	200

[a]Indicates whether the heterocyclic base was taken in stoichiometric amount (S.a.) or in excess.

the contents had been stirred for another two hours and then cooled. The separated product was filtered in a G_4 filtration unit, washed with acetone and diethyl ether, dried under vacuum and placed in a desiccator containing anhydrous calcium chloride.
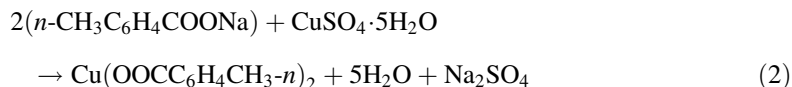
Elemental Analyses and Physical Measurements

Copper in the complexes was determined volumetrically by EDTA titration using xylenol orange as indicator. Carbon and hydrogen analyses were performed on an automatic Coleman-33 analyser, while nitrogen was determined by Kjeldahl's method in the departmental microanalytical laboratory.

Infrared spectra of the copper(II) toluate (*ortho*-, *meta*- and *para*-) complexes with the heterocyclic bases, and their anhydrous sodium toluates were recorded as KBr pellets on a Pye Unicam SP3-300 infrared spectrophotometer in the $4000–200$ cm^{-1} region. Electronic reflectance spectra of the complexes (either neat or diluted with an appropriate amount of $MgCO_3$) were recorded on a Unicam SP-700 UV-Vis. spectrophotometer having a SP-735 diffuse reflectance attachment ($50,000–4000$ cm^{-1}). The X-band EPR measurements ($9.439–9.442$ GHz) of powdered samples at room temperature were made on a JES-FE3XG electron paramagnetic resonance spectrometer while the X-band EPR measurements ($8.916–9.190$ GHz) of powdered samples of three complexes at different temperatures were made on a Varian E-4 electron paramagnetic resonance spectrometer. Diphenylpicrylhydrazyl (DPPH) was used as calibrant. The room temperature magnetic susceptibility of all of the complexes was measured on a Gouy balance using $Hg[Co(NCS)_4]$ as calibrant.

RESULTS AND DISCUSSION

Copper(II) toluates were prepared by reacting aqueous solution of copper(II) sulfate with stoichiometric amounts of sodium salts of the corresponding toluic acids in 1:1 water–acetone mixture. The synthesis of the adducts of copper(II) toluates with substituted piperidines was performed by reacting their diethyl ether solutions in 1:05; 1:1 and 50% excess of stoichiometric amounts of the bases whereby only complexes of the 1:1 stoichiometry were obtained by the following equations.

$$n\text{-}CH_3C_6H_4COOH + NaOH \rightarrow n\text{-}CH_3C_6H_4COONa + H_2O \qquad (1)$$

$$2(n\text{-}CH_3C_6H_4COONa) + CuSO_4 \cdot 5H_2O$$

$$\rightarrow Cu(OOCC_6H_4CH_3\text{-}n)_2 + 5H_2O + Na_2SO_4 \qquad (2)$$

$$Cu(OOCC_6H_4CH_3\text{-}n)_2 + L \rightarrow Cu(OOCC_6H_4CH_3\text{-}n)_2L \qquad (3)$$

where n = 2, 3 or 4 and L = 1-PePip, 1-EtPipd and 2,6-Me$_2$Pipd.

The complexes are insoluble in organic solvents and do not melt, but decompose above 250 °C. The interest in the present investigations was to see the role of pK_a of the parent carboxylic acid on the structure and the effect of steric and electronic properties of the six-membered saturated monoheterocyclic bases on the stoichiometry, magnetic behaviour and structure of the complexes. Chemical formulae based upon elemental analyses, colour and particulars of the method of preparation of complexes are listed in Table 1.

IR Spectral Studies

The structural possibilities for complexes of the stoichiometry Cu(OOCR)$_2$L depend upon the mode of coordination of the carboxylate group and the monoheterocyclic bases, the substituted piperidines. IR studies are quite useful in determining the mode of coordination of these ligands.[5] Examination of the positions and direction of the shifts of the ν_a(OCO) and ν_s(OCO) bands of the carboxylate group in the complexes as compared to their positions in sodium toluates (Table 2), suggests a bridging bidentate mode of coordination of the carboxylate group for all of the complexes.[11] Additional bands in the complexes, by comparison with the IR spectra of uncomplexed copper(II) toluates and free bases in the regions 410–465 cm^{-1} and 275–320 cm^{-1}, tentatively have been assigned to ν(Cu–O) and ν(Cu–N) modes, respectively.[12–16]

Table 2. Some coordinatively diagnostic features of infrared spectra (cm^{-1}) of the sodium salts of carboxylic acids and their copper(II) complexes.

Compound	ν_a(OCO)	ν_s(OCO)	ν(Cu–O)	ν(Cu–N)
Cu(OOCC$_6$H$_4$CH$_3$-4)$_2$(1-MePipd)	1562 s	1408 vs	450 m	305 s
Cu(OOCC$_6$H$_4$CH$_3$-4)$_2$(1-EtPipd)	1598 s	1408 vs	458 m	315 s
Cu(OOCC$_6$H$_4$CH$_3$-4)$_2$(2,6-Me$_2$Pipd)	1580 s	1408 vs	450 m	300 s
Cu(OOCC$_6$H$_4$CH$_3$-3)$_2$(1-MePipd)	1573 s	1415 vs	420 m	275 s
Cu(OOCC$_6$H$_4$CH$_3$-3)$_2$(1-EtPipd)	1585 s	1402 vs	410 m	290 s
Cu(OOCC$_6$H$_4$CH$_3$-3)$_2$(2,6-Me$_2$Pipd)	1580 s	1410 vs	430 m	320 s
Cu(OOCC$_6$H$_4$CH$_3$-2)$_2$(1-EtPipd)	1560 s	1420 vs	465 m	305 s
4-CH$_3$C$_6$H$_4$COONa	1545 s	1406 vs		
3-CH$_3$C$_6$H$_4$COONa	1560 s	1405 vs		
2-CH$_3$C$_6$H$_4$COONa	1515 s	1403 vs		

Table 3. Electronic reflectance spectral data (cm^{-1}) and room temperature μ_{eff} values of the antiferromagnetic copper(II) toluates with substituted piperidines.

Compound	Absorption I d–d transitions	Absorption II ligand → metal charge transfer transitions	μ_{eff} (B.M.)
$Cu(OOCC_6H_4CH3-4)2(1-MePipd)$	13,890	35,715	1.353
$Cu(OOCC_6H_4CH_3-4)_2(1-EtPipd)$	13,795	37,035	1.493
$Cu(OOCC_6H_4CH_3-4)_2(2,6-Me_2Pipd)$	13,795	37,035	1.432
$Cu(OOCC_6H_4CH_3-3)_2(1-MePipd)$	13,605	32,260	1.387
$Cu(OOCC_6H_4CH_3-3)_2(1-EtPipd)$	13,515	33,335	1.516
$Cu(OOCC_6H_4CH_3-3)_2(2,6-Me_2Pipd)$	13,985	33,335	1.452
$Cu(OOCC_6H_4CH_3-2)_2(1-EtPipd)$	13,335	33,335	1.638

Electronic Reflectance Spectral Studies

Two absorptions (Table 3), one as a broad band in the region 13,985–13,335 cm^{-1} (band I) and the other as a shoulder around 32,260–37,035 cm^{-1} (band II), are observed for all of the complexes under study. Band I may be due to the absorption corresponding to the $d_{xy} \rightarrow d_{x^2-y^2}$ and d_{xz}, $d_{yz} \rightarrow d_{x^2-y^2}$ electronic transitions for the copper(II) ion in tetragonal environments.[17] The band II can be assigned to the $2p_\pi(O) \rightarrow (d_{x^2-y^2})^*$. *The star is put to indicate the antibonding nature of the $d_{x^2-y^2}$ orbital charge-transfer transition; the appearance of this band is considered to be characteristic of the dimeric structure for copper(II) carboxylate complexes.[17–19]

EPR Studies

The X-band room temperature EPR spectra of powdered samples of all the complexes under discussion exhibit three electron paramagnetic resonance absorption lines at the field strengths 600 G, 4700 G and 6100 G, which are characteristic of the spin-triplet state (S = 1) in the axial symmetry of binuclear complexes and correspond, respectively, to the resonance fields H_{z1}, $H_\perp$ and H_{z2} with D > hv and E = 0,[20,21] the zero field splitting parameters for a triplet state. That these complexes do not seem to undergo rhombic distortion, is confirmed by the absorption line at 4700 G ($H_\perp$) not being split even at low temperatures. The range of the electron paramagnetic resonance parameters $g_\parallel$ or g_z (2.41–2.5), $g_\perp$ (2.10–2.12) and D (0.37–0.39) (Table 4), as evaluated from the EPR spectra, are

Table 4. Electron paramagnetic resonance spectral parameters, values of spin exchange parameter, $-2J$ (cm^{-1}), of antiferromagnetic copper(II) complexes and pK_a of axial ligand and carboxylic acid.

Compound	$g_\perp$	$g_\parallel$	g_{av}	$(D)\ cm^{-1}$	Carboxylic acid pK_a	Axial ligand pK_a	$-2J$
Cu(OOCC$_6$H$_4$CH$_3$-4)$_2$(1-MePipd)	2.1195	2.4520	2.2306	0.3778			
Cu(OOCC$_6$H$_4$CH$_3$-4)$_2$(1-EtPipd)	2.1079	2.4871	2.2343	0.3760	4.367	10.450	281 ± 11
Cu(OOCC$_6$H$_4$CH$_3$-4)$_2$(2,6-Me$_2$Pipd)	2.0989	2.4352	2.2110	0.3673			
Cu(OOCC$_6$H$_4$CH$_3$-3)$_2$(1-MePipd)	2.1159	2.4355	2.2224	0.3900			
Cu(OOCC$_6$H$_4$CH$_3$-3)$_2$(1-EtPipd)	2.1184	2.4091	2.2153	0.3712	4.252	10.450	273 ± 11
Cu(OOCC$_6$H$_4$CH$_3$-3)$_2$(2,6-MePipd)	2.1237	2.4308	2.2261	0.3717			
Cu(OOCC$_6$H$_4$CH$_3$-2)$_2$(1-EtPipd)	2.1030	2.4308	2.2123	0.3831	3.870	10.450	305 ± 8
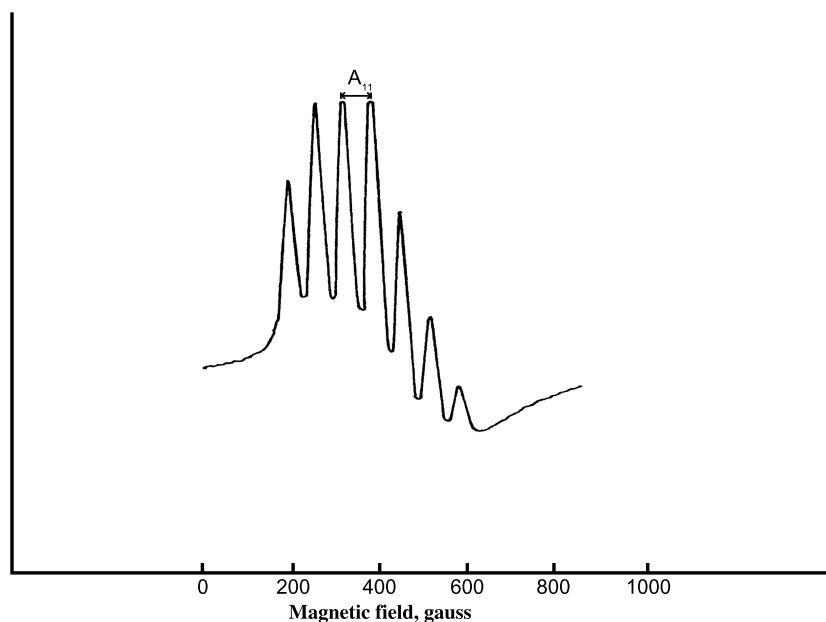
Figure 1. Electron paramagnetic resonance spectrum of $[Cu(OOCC_6H_4CH_3-4)_2-(1\text{-EtPipd})]$ at 113 K.

comparable with the earlier reported values for binuclear copper(II) carboxylate complexes.[4-7] In the complex $Cu(OOCC_6H_4CH_3-4)_2(1\text{-EtPipd})$ at low temperature (113 K) the electron paramagnetic resonance absorption band around 600 G (H_{z1}) is split into seven lines having an intensity ratio of 1:2:3:4:3:2:1 due to hyperfine coupling of the nuclear spin of two copper ions with the electron spin ($2nI + 1$ lines; $n = 2$ and $I = 3/2$ for ^{63}Cu) (Figure 1). The observed value of $A_{\parallel}$ is found to be about one half (0.006968 cm^{-1}) of that generally observed for magnetically dilute copper(II) complexes in similar environments. The value of $A_{\parallel}$ lies close to the values reported earlier[21,22] for binuclear copper(II) carboxylate complexes. This observation further supports the magnetic exchange-taking place between two metal ions[21,22] (in spin–spin coupled complexes). In addition to the above-mentioned absorptions, an absorption line around 3200 G is also observed. The intensity of this line increases while the intensity of the lines due to the triplet state, as expected, decreases on lowering of the temperature. This line is, therefore, attributed to the magnetically dilute

copper(II) impurity which is commonly present in copper(II) arylcarboxylate complexes.[20,23,24]

Magnetic Susceptibility Studies

The room-temperature μ_{eff} values for all of the copper(II) complexes lie in the range 1.35–1.64 B.M. (Table 3) which is less than the spin-only value for one unpaired electron (1.73). These values are, however, close to the values reported for dinuclear or polynuclear copper(II) carboxylate complexes in which the carboxylate group is acting as a bridge between two metal ions[6,7,13] and spin–spin interaction exists. For three complexes the value of the spin exchange parameter (−2J) has been calculated from the variation of the intensity (I) of the EPR lines at the temperatures 223, 173 and 113 K using the relation of Eq. 4.[20,24]

$$\frac{A_1}{A_2} = \frac{I_1}{I_2} = \frac{T_2(3 + e^{-2J/kT_2})}{T_1(3 + e^{-2J/kT_1})} \tag{4}$$

The relative areas of the curves [A_1/A_2] at two different temperatures (T_1 and T_2) were calculated by the reported methods.[25] Uncertainties in the values of −2J by this method are ±11 cm^{-1}. The EPR method, although it is free from the presence of the magnetic impurity as compared to the magnetic susceptibility method for calculating −2J, suffers from the limitation in evaluating the accurate areas under the EPR curves. The values of −2J (Table 3) are comparable to those for the earlier reported copper(II) carboxylate complexes with terminal ligands of low basicity, *e.g.* pyridine, etc.

For all of the complexes under study which exhibit antiferromagnetic behaviour, a copper(II) acetate monohydrate-like dinuclear structure[26] (Figure 2) may be assigned.

The literature[6,7] reveals that the variation of −2J values with the properties of the terminal ligand is not a simple function of the donor strength of the ligand or any other readily recognizable parameter. The study of antiferromagnetic interactions in the copper(II) arylcarboxylate complexes had been considered to be of special interest since a predictable variation in the electron donor properties of the arylcarboxylate group can be effected much more easily by varying the substituent and its position on the aryl ring. However, attempts at arriving at a firm correlation between −2J values and the donor ability of the arylcarboxylate anion or the pK_a of the parent acid have been disappointing which, in view of the earlier reports, is not surprising.[5] This is partly because, in general, −2J values
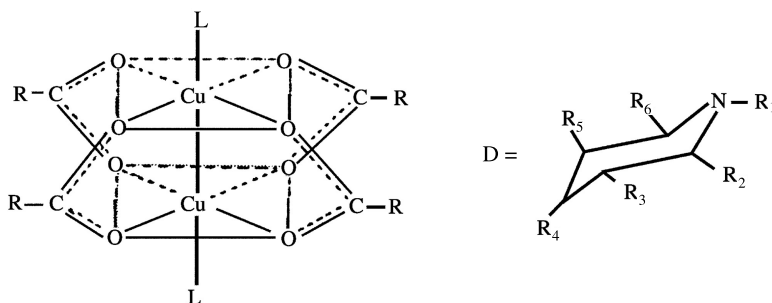
R = 2-; 3-; 4-$CH_3C_6H_4$
L = 1-Methylpiperidine or 1-Ethylpiperidine: R_1 = CH_3 or C_2H_5; $R_2 = R_3 = R_4 = R_5 = R_6$ = H
= 2,6-Dimethylpipridine: $R_2 = R_6 = CH_3$; $R_1 = R_3 = R_4 = R_5$ = H

Figure 2. Proposed structure for the complexes Cu(OOCR)$_2$L.

for arylcarboxylates are lower than those of alkylcarboxylates and the data for reasons like limitations in the availability of resources are imprecise.[4,5] Consequently, the variation in $-2J$ values for the complexes for which these have been determined is small and the differences may well be of the order of the experimental error.

The general lack of correlation between the extent of antiferromagnetic interaction and the pK$_a$'s and the donor strength of the ligands (terminal ligand and the bridging carboxylate) may be explained as follows: Firstly, in view of the well-known concept of soft and hard acids and bases[26] and Drago and Wayland's[27] two-parameter model for acids and bases, it is not proper to assume that the donor ability toward a particular acceptor of different types of ligands will follow the trend expected from the pK$_a$ values of the ligands or the parent acids. Since the pK$_a$ values are determined by the ability of the donor atoms for protons only, only ligands having similar donor atoms and an electronic charge on them, with similar steric and other electronic characteristics, can be compared as regards the interactions with a particular metal in a complex. The reason for this is that here the acceptor (metal ion) has particular electronic characteristics and stringent steric requirements. Secondly, even if it is assumed that the donor ability of the ligands is determined only by their pK$_a$'s, the larger amount of charge transferred to the copper ions by the ligands considered to be stronger donors on this basis may not lead to larger antiferromagnetic interactions. While expecting a correlation between donor strength and $-2J$ values in copper(II) complexes, it is assumed that a greater electronic charge transferred by a stronger donor would result in a smaller residual

positive charge on copper ions and a greater expansion and overlap of the d orbitals containing unpaired electrons in a metal–metal direct interaction. However, these days, indirect exchange is considered to be the predominant mechanism, which does not seem to require expansion of d orbitals for adequate overlap with ligand orbitals. Moreover, the stronger linkage of a bridging ligand will push $d_{x^2-y^2}$ orbitals on copper(II) to a higher energy level and thus cause the degree of mixing of d_{xy*} orbitals into $d_{x^2-y^2}$ orbitals (which contain unpaired electrons) to be diminished. This will lead to a reduction in the indirect exchange interaction and consequent diminution in antiferromagnetic interaction, since the indirect exchange takes place largely through interaction of the delocalized π-bonding framework of the bridging carboxylates with d_{xy*} orbitals of the metal ions.[28] The smooth correlations observed/claimed in a few cases, especially for the bridging ligand, could just be fortuitous.

CONCLUSIONS

Our interest in the present work was to study the complexation behaviour of saturated monoheterocyclic bases of different but high basicities and different steric characteristics with copper(II) carboxylates. An additional interest was to see whether these bases form magnetically dilute or antiferromagnetic complexes. In the present study all the complexes have been found to be antiferromagnetic. The results of analysis show that only complexes with 1:1 stoichiometry were obtained and that the steric hindrance of the amine ligands plays an important role in determining the stoichiometry, structure and, hence, the magnetic properties of the complexes.

REFERENCES

1. Kato, M.; Jonassen, H.B.; Fanning, J.C. Copper(II) complexes with subnormal magnetic moments. Chem. Rev. **1964**, *64*, 99–125 and refs therein.
2. Oldham, C. Complexes of simple carboxylic acids. In *Progress in Inorganic Chemistry*; Interscience Publications: New York, 1968; Vol. 10, 223–250.
3. Doedens, R.J. Structure and metal interactions in copper(II) carboxylate complexes. In *Progress in Inorganic Chemistry*; Interscience Publications: New York, 1976; Vol. 21, 209–229.
4. Jotham, R.W.; Kettle, S.F.A.; Marks, J.A. Antiferromagnetism in

transition metal complexes. Part IV: low-lying excited states of bi-
nuclear copper(II) carboxylate complexes. J. Chem. Soc., Dalton Trans.
1972, 428.

5. Catterick, J.; Thornton, P. Structures and physical properties of
    polynuclear carboxylates. In *Advanced Inorganic Chemistry and
    Radiochemistry*; Academic Press: New York, 1977; Vol. 20, 291–350
    and references therein.

6. Melnik, M. Mono-, bi-, tetra- and polynuclear copper(II) halogen-
    carboxylates. Coord. Chem. Rev. **1981**, *36*, 1–40.

7. Melnik, M. Study of the relation between the structural data and
    magnetic interaction in oxo-bridged binuclear copper(II) complexes.
    Coord. Chem. Rev. **1982**, *42*, 259–289.

8. Catterick, J.; Thornton, P. Synthesis, magnetic properties and electronic
    spectra of complexes of Ni(II) carboxylates with pyridine and related
    ligands. J. Chem. Soc., Dalton Trans. **1975**, 233–238.

9. Catterick, J.; Thorton, P. Mononuclear and polynuclear complexes of
    cobalt(II) carboxylates with pyridine and other heterocyclic bases. J.
    Chem. Soc., Dalton Trans. **1976**, 1634–1640.

10. Bencini, A.; Benelli, C.; Gatteschi, D.; Zanchini, C. Exchange
    interactions in copper(II)–nickel(II) and nickel(II)–nickel(II) pairs in
    tetra(μ-benzoato-O,O′)bis((quinoline)-dimetal(II) complexes. J. Am.
    Chem. Soc. **1980**, *102*, 5820–5823.

11. Manhas, B.S.; Trikha, A.K. Relationship between the direction of shifts
    in the carbon–oxygen stretching frequencies of carboxylato complexes
    and the type of carboxylate coordination. J. Indian Chem. Soc. **1982**,
    59, 315–319.

12. Battaglia, L.P.; Corradi, B.A.; Palmieri, G.C. Bisacetatobismorpho-
    linecopper(II) dihydrate, $C_{12}H_{28}CuN_2O_8$. Cryst. Struct. Commun. **1973**,
    2, 523–525.

13. Marcotrigiano, G.; Pellacani, G.C.; Preti, C. Acetato- and propianato-
    (saturated heterocyclic) amine complexes of cobalt(II), nickel(II) and
    copper(II). Z. Anorg. Allg. Chem. **1974**, *408*, 313–320.

14. Marcotrigiano, G.; Battistuzzi, R.; Pellacani, G.C. Adducts of
    piperidine, piperazine, methylpiperazine and morpholine with bis(β-
    ketoenolates) of nickel(II). Can. J. Chem. **1972**, *50*, 2557–2560.

15. Kumar, N.; Kachroo, P.L.; Kant, R. Studies on complexes of metal(II)
    carboxylates with donor molecules. Part III. Complexes of cobalt(II)
    alkanoates with aromatic amine N-oxides. Trans Met. Chem. **1974**, *4*,
    315–318.

16. Battaglia, L.P.; Bonamartini, C.A.; Marcotrigiano, G.; Menaube, L.;
    Pellacani, G.C. Synthesis and spectroscopic and structural properties of
    bis(N-acetyl-DL-tryptophanato)copper(II) complex and its amine

adducts. Effect of amines on the amino acid coordination. Crystal and molecular structure of diaquabis(N-acrtyl-DL-tryptophanato)bis(pyridine)copper(II). J. Am. Chem. Soc. **1980**, *102*, 2663–2669.

17. Dubicki, L. Electronic spectrum of binuclear-copper acetate monohydrate. Aus. J. Chem. **1972**, *25*, 1141.

18. Dubicki, L.; Martin, R.L. The μ-system of binuclear copper(II) and chromium(II) acetates. Inorg. Chem. **1966**, *5*, 2203–2209.

19. Kida, S.; Nishida, Y.; Sakamoto, M. Absorption band in the near-ultraviolet region observed for binuclear copper(II) complexes. Bull. Chem. Soc. Jpn. **1973**, *46*, 2428–2430.

20. Wasson, J.R.; Shyr, C.; Trapp, C. The spectral and magnetic properties of copper(II) cyanoacetate. Inorg. Chem. **1968**, *7*, 469–473.

21. Smith, T.D.; Pillbrow, J.R. Determination of structural properties of dimeric transition ion complexes from EPR spectra. Coord. Chem. Rev. **1974**, *5*, 173–278.

22. Kokoszka, G.F.; Duerst, R.W. EPR studies of exchange coupled metal ions. Coord. Chem. Rev. **1970**, *5*, 209–244.

23. Thompson, R.C.; Herring, F.G.; Landa, B.; Schwerdtfeger, C.F. Magnetic susceptibility and electron spin resonance studies on amine-copper(II) arylcarboxylates. J. Chem. Soc., A **1971**, 528–535.

24. Newton, W.J.; Oldman, C.; Tabner, B.J. Magnetic susceptibility and electron spin resonance of some copper(II) unsaturated carboxylates. J. Chem. Soc. Dalton Trans. **1980**, 1379–1382.

25. Wertz, J.E.; Bolton, J.R. *Electron Spin Resonance, Elementary Theory and Practical Applications*; McGraw-Hill: New York, 1972; 32.

26. Pearson, R.G. Hard and soft acids and bases. J. Am. Chem. Soc. **1963**, *85*, 3533–3539.

27. Drago, R.S.; Wayland, B.B. A double-scale equation for correlating enthalpies of Lewis acid–base interactions. J. Am. Chem. Soc. **1965**, *87*, 3571–3577.

28. Gerloch, M.; Harding, J.H. Superexchange in copper acetates. Proc. R. Soc. Lond., A **1978**, *360*, 211.